Galerkin AX

August 22, 2007

1 Equations

1.1 Mass conservation

$$\frac{\partial c_i}{\partial t} = -\vec{\nabla}.\vec{N}_i + R_i \tag{1}$$

with

$$\vec{N}_i = c_i\vec{v} - \sum_j D_{ij}\vec{\nabla}c_j - w_i c_i \vec{\nabla}U \tag{2}$$

1.2 Poisson's equation

$$\vec{\nabla}^2 U + \frac{F}{\epsilon}\sum_i z_i c_i = 0 \tag{3}$$

1.3 Butler-Volmer kinetics

$$v = k_{ox}\exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right]c_{red} - k_{red}\exp\left[-\frac{\alpha_{red} nF}{RT}(V-U)\right]c_{ox} \tag{4}$$

2 Element matrix

Note

$$\vec{\nabla}N^m = \frac{\vec{n}^m}{2S}$$

2.1 Convection

2.1.1 Fluctuation in node

$$\Delta c_i^m = \int_S -\vec{v}.\vec{\nabla}c_i N^m r dS$$

2.1.2 Element contribution to fluctuation in node

Assume that $\vec{v}$ varies linearly.

$$\mathcal{R}^{11} = 6r^1 + 2r^2 + 2r^3$$

$$\mathcal{R}^{22} = 2r^1 + 6r^2 + 2r^3$$

$$\mathcal{R}^{33} = 2r^1 + 2r^2 + 6r^3$$

$$\mathcal{R}^{12} = \mathcal{R}^{21} = 2r^1 + 2r^2 + r^3$$

$$\mathcal{R}^{13} = \mathcal{R}^{31} = 2r^1 + r^2 + 2r^3$$

$$\mathcal{R}^{23} = \mathcal{R}^{32} = r^1 + 2r^2 + 2r^3$$

$$\vec{\mathcal{V}}^1 = \mathcal{R}^{11}\vec{v}^1 + \mathcal{R}^{12}\vec{v}^2 + \mathcal{R}^{13}\vec{v}^3$$

$$\vec{\mathcal{V}}^2 = \mathcal{R}^{21}\vec{v}^1 + \mathcal{R}^{22}\vec{v}^2 + \mathcal{R}^{23}\vec{v}^3$$

$$\vec{\mathcal{V}}^3 = \mathcal{R}^{31}\vec{v}^1 + \mathcal{R}^{32}\vec{v}^2 + \mathcal{R}^{33}\vec{v}^3$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \end{array} \right\} = \frac{1}{120} \left[\begin{array}{ccc} \vec{\mathcal{V}}^1.\vec{n}^1 & \vec{\mathcal{V}}^1.\vec{n}^2 & \vec{\mathcal{V}}^1.\vec{n}^3 \\ \vec{\mathcal{V}}^2.\vec{n}^1 & \vec{\mathcal{V}}^2.\vec{n}^2 & \vec{\mathcal{V}}^2.\vec{n}^3 \\ \vec{\mathcal{V}}^3.\vec{n}^1 & \vec{\mathcal{V}}^3.\vec{n}^2 & \vec{\mathcal{V}}^3.\vec{n}^3 \end{array} \right] \left\{ \begin{array}{c} c_i^1 \\ c_i^2 \\ c_i^3 \end{array} \right\} \tag{5}$$

2.1.3 Examples: binary electrolyte

$$\left\{ \begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \\ \Delta c_A^3 \\ \Delta c_B^3 \\ \Delta U^3 \end{array} \right\} = \left[\begin{array}{ccccccccc} V^{11} & 0 & 0 & V^{12} & 0 & 0 & V^{13} & 0 & 0 \\ 0 & V^{11} & 0 & 0 & V^{12} & 0 & 0 & V^{13} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ V^{21} & 0 & 0 & V^{22} & 0 & 0 & V^{23} & 0 & 0 \\ 0 & V^{21} & 0 & 0 & V^{22} & 0 & 0 & V^{23} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ V^{31} & 0 & 0 & V^{32} & 0 & 0 & V^{33} & 0 & 0 \\ 0 & V^{31} & 0 & 0 & V^{32} & 0 & 0 & V^{33} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{array} \right] \left\{ \begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \\ c_A^3 \\ c_B^3 \\ U^3 \end{array} \right\} \tag{6}$$

$$V^{mn} = \frac{\vec{\mathcal{V}}^m.\vec{n}^n}{120}$$

2.2 Diffusion

2.2.1 Fluctuation in node

$$\begin{aligned}\Delta c_i^m &= \int_S \vec{\nabla}.\left(\sum_j D_{ij}\vec{\nabla}c_j\right)N^m r dS \\ &= -\int_S \left(\sum_j D_{ij}\vec{\nabla}c_j\right).\vec{\nabla}N^m r dS\end{aligned}$$

2.2.2 Element contribution to fluctuation in node

Assume that D_{ij} varies linearly.

$$\mathcal{R}^1 = 2r^1 + r^2 + r^3$$

$$\mathcal{R}^2 = r^1 + 2r^2 + r^3$$

$$\mathcal{R}^3 = r^1 + r^2 + 2r^3$$

$$\left\{\begin{array}{c}\Delta c_i^1\\ \Delta c_i^2\\ \Delta c_i^3\end{array}\right\} = -\sum_j \frac{\mathcal{R}^1 D_{ij}^1 + \mathcal{R}^2 D_{ij}^2 + \mathcal{R}^3 D_{ij}^3}{48S}\left[\begin{array}{ccc}\vec{n}^1.\vec{n}^1 & \vec{n}^1.\vec{n}^2 & \vec{n}^1.\vec{n}^3\\ \vec{n}^2.\vec{n}^1 & \vec{n}^2.\vec{n}^2 & \vec{n}^2.\vec{n}^3\\ \vec{n}^3.\vec{n}^1 & \vec{n}^3.\vec{n}^2 & \vec{n}^3.\vec{n}^3\end{array}\right]\left\{\begin{array}{c}c_j^1\\ c_j^2\\ c_j^3\end{array}\right\} \tag{7}$$

2.2.3 Example: binary electrolyte

$$\left\{\begin{array}{c}\Delta c_A^1\\ \Delta c_B^1\\ \Delta U^1\\ \Delta c_A^2\\ \Delta c_B^2\\ \Delta U^2\\ \Delta c_A^3\\ \Delta c_B^3\\ \Delta U^3\end{array}\right\} = \left[\begin{array}{ccccccccc}D_{AA}^{11} & D_{AB}^{11} & 0 & D_{AA}^{12} & D_{AB}^{12} & 0 & D_{AA}^{13} & D_{AB}^{13} & 0\\ D_{BA}^{11} & D_{BB}^{11} & 0 & D_{BA}^{12} & D_{BB}^{12} & 0 & D_{BA}^{13} & D_{BB}^{13} & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\ D_{AA}^{21} & D_{AB}^{21} & 0 & D_{AA}^{22} & D_{AB}^{22} & 0 & D_{AA}^{23} & D_{AB}^{23} & 0\\ D_{BA}^{21} & D_{BB}^{21} & 0 & D_{BA}^{22} & D_{BB}^{22} & 0 & D_{BA}^{23} & D_{BB}^{23} & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\ D_{AA}^{31} & D_{AB}^{31} & 0 & D_{AA}^{32} & D_{AB}^{32} & 0 & D_{AA}^{33} & D_{AB}^{33} & 0\\ D_{BA}^{31} & D_{BB}^{31} & 0 & D_{BA}^{32} & D_{BB}^{32} & 0 & D_{BA}^{33} & D_{BB}^{33} & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\end{array}\right]\left\{\begin{array}{c}c_A^1\\ c_B^1\\ U^1\\ c_A^2\\ c_B^2\\ U^2\\ c_A^3\\ c_B^3\\ U^3\end{array}\right\} \tag{8}$$

with

$$D_{ij}^{mn} = -\frac{\mathcal{R}^1 D_{ij}^1 + \mathcal{R}^2 D_{ij}^2 + \mathcal{R}^3 D_{ij}^3}{48S}\vec{n}^m.\vec{n}^n$$

2.3 Migration

2.3.1 Fluctuation in node

$$\begin{aligned}\Delta c_i^m &= \int_S \vec{\nabla}.\left(w_i c_i \vec{\nabla}U\right)N^m r dS \\ &= -\int_S \left(w_i c_i \vec{\nabla}U\right).\vec{\nabla}N^m r dS\end{aligned}$$

2.3.2 Element contribution to fluctuation in node

Assume that w_i varies linearly.

$$\mathcal{R}^{11} = 6r^1 + 2r^2 + 2r^3$$

$$\mathcal{R}^{22} = 2r^1 + 6r^2 + 2r^3$$

$$\mathcal{R}^{33} = 2r^1 + 2r^2 + 6r^3$$

$$\mathcal{R}^{12} = \mathcal{R}^{21} = 2r^1 + 2r^2 + r^3$$

$$\mathcal{R}^{13} = \mathcal{R}^{31} = 2r^1 + r^2 + 2r^3$$

$$\mathcal{R}^{23} = \mathcal{R}^{32} = r^1 + 2r^2 + 2r^3$$

$$\mathcal{W}_i^1 = \mathcal{R}^{11} w_i^1 + \mathcal{R}^{12} w_i^2 + \mathcal{R}^{13} w_i^3$$

$$\mathcal{W}_i^2 = \mathcal{R}^{21} w_i^1 + \mathcal{R}^{22} w_i^2 + \mathcal{R}^{23} w_i^3$$

$$\mathcal{W}_i^3 = \mathcal{R}^{31} w_i^1 + \mathcal{R}^{32} w_i^2 + \mathcal{R}^{33} w_i^3$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \end{array} \right\} = -\frac{\mathcal{W}_i^1 c_i^1 + \mathcal{W}_i^2 c_i^2 + \mathcal{W}_i^3 c_i^3}{240S} \left[\begin{array}{ccc} \vec{n}^1.\vec{n}^1 & \vec{n}^1.\vec{n}^2 & \vec{n}^1.\vec{n}^3 \\ \vec{n}^2.\vec{n}^1 & \vec{n}^2.\vec{n}^2 & \vec{n}^2.\vec{n}^3 \\ \vec{n}^3.\vec{n}^1 & \vec{n}^3.\vec{n}^2 & \vec{n}^3.\vec{n}^3 \end{array} \right] \left\{ \begin{array}{c} U^1 \\ U^2 \\ U^3 \end{array} \right\} \tag{9}$$

2.3.3 Example: binary electrolyte

$$\left\{ \begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \\ \Delta c_A^3 \\ \Delta c_B^3 \\ \Delta U^3 \end{array} \right\} = \left[\begin{array}{ccccccccc} 0 & 0 & M_A^{11} & 0 & 0 & M_A^{12} & 0 & 0 & M_A^{13} \\ 0 & 0 & M_B^{11} & 0 & 0 & M_B^{12} & 0 & 0 & M_B^{13} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & M_A^{21} & 0 & 0 & M_A^{22} & 0 & 0 & M_A^{23} \\ 0 & 0 & M_B^{21} & 0 & 0 & M_B^{22} & 0 & 0 & M_B^{23} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & M_A^{31} & 0 & 0 & M_A^{32} & 0 & 0 & M_A^{33} \\ 0 & 0 & M_B^{31} & 0 & 0 & M_B^{32} & 0 & 0 & M_B^{33} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{array} \right] \left\{ \begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \\ c_A^3 \\ c_B^3 \\ U^3 \end{array} \right\} \tag{10}$$

with

$$M_i^{mn} = -\frac{\mathcal{W}_i^1 c_i^1 + \mathcal{W}_i^2 c_i^2 + \mathcal{W}_i^3 c_i^3}{240S} \vec{n}^m.\vec{n}^n$$

2.4 Homogeneous reactions

2.4.1 Fluctuation in node

$$R_i = \sum_r s_{i,r} v_r$$

- Monomolecular

$$v = kc_j$$

$$\Delta c_i^m = \int_S kc_j N^m r dS$$

- Bimolecular

$$v = kc_j c_k$$

$$\begin{aligned}\Delta c_i^m &= \int_S kc_j c_k N^m r dS \\ &= \tfrac{1}{2}\int_S kc_k c_j N^m r dS + \tfrac{1}{2}\int_S kc_j c_k N^m r dS\end{aligned}$$

2.4.2 Element contribution to fluctuation in node

Assume that k varies linearly.

- Monomolecular

$$\mathcal{R}^{111} = 12r^1 + 3r^2 + 3r^3$$

$$\mathcal{R}^{222} = 3r^1 + 12r^2 + 3r^3$$

$$\mathcal{R}^{333} = 3r^1 + 3r^2 + 12r^3$$

$$\mathcal{R}^{112} = \mathcal{R}^{121} = \mathcal{R}^{211} = 3r^1 + 2r^2 + r^3$$

$$\mathcal{R}^{113} = \mathcal{R}^{131} = \mathcal{R}^{311} = 3r^1 + r^2 + 2r^3$$

$$\mathcal{R}^{221} = \mathcal{R}^{122} = \mathcal{R}^{212} = 2r^1 + 3r^2 + r^3$$

$$\mathcal{R}^{223} = \mathcal{R}^{232} = \mathcal{R}^{322} = r^1 + 3r^2 + 2r^3$$

$$\mathcal{R}^{331} = \mathcal{R}^{133} = \mathcal{R}^{313} = 2r^1 + r^2 + 3r^3$$

$$\mathcal{R}^{332} = \mathcal{R}^{233} = \mathcal{R}^{323} = r^1 + 2r^2 + 3r^3$$

$$\mathcal{R}^{123} = \mathcal{R}^{213} = \mathcal{R}^{132} = \mathcal{R}^{312} = \mathcal{R}^{231} = \mathcal{R}^{321} = r^1 + r^2 + r^3$$

$$\mathcal{H}_j^{11} = \mathcal{R}^{111}k^1 + \mathcal{R}^{112}k^2 + \mathcal{R}^{113}k^3$$

$$\mathcal{H}_j^{22} = \mathcal{R}^{221}k^1 + \mathcal{R}^{222}k^2 + \mathcal{R}^{223}k^3$$

$$\mathcal{H}_j^{33} = \mathcal{R}^{331}k^1 + \mathcal{R}^{332}k^2 + \mathcal{R}^{333}k^3$$

$$\mathcal{H}_j^{12} = \mathcal{H}_j^{21} = \mathcal{R}^{121}k^1 + \mathcal{R}^{122}k^2 + \mathcal{R}^{123}k^3$$

$$\mathcal{H}_j^{13} = \mathcal{H}_j^{31} = \mathcal{R}^{131}k^1 + \mathcal{R}^{132}k^2 + \mathcal{R}^{133}k^3$$

$$\mathcal{H}_j^{23} = \mathcal{H}_j^{32} = \mathcal{R}^{231}k^1 + \mathcal{R}^{232}k^2 + \mathcal{R}^{233}k^3$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \end{array} \right\} = \frac{S}{180} \left[\begin{array}{ccc} \mathcal{H}_j^{11} & \mathcal{H}_j^{12} & \mathcal{H}_j^{13} \\ \mathcal{H}_j^{21} & \mathcal{H}_j^{22} & \mathcal{H}_j^{23} \\ \mathcal{H}_j^{31} & \mathcal{H}_j^{32} & \mathcal{H}_j^{33} \end{array} \right] \left\{ \begin{array}{c} c_j^1 \\ c_j^2 \\ c_j^3 \end{array} \right\} \tag{11}$$

- Bimolecular

$$\mathcal{R}^{1111} = 60r^1 + 12r^2 + 12r^3$$

$$\mathcal{R}^{2222} = 12r^1 + 60r^2 + 12r^3$$

$$\mathcal{R}^{3333} = 12r^1 + 12r^2 + 60r^3$$

$$\mathcal{R}^{1112} = \mathcal{R}^{1121} = \mathcal{R}^{1211} = \mathcal{R}^{2111} = 12r^1 + 6r^2 + 3r^3$$

$$\mathcal{R}^{1113} = \mathcal{R}^{1131} = \mathcal{R}^{1311} = \mathcal{R}^{3111} = 12r^1 + 3r^2 + 6r^3$$

$$\mathcal{R}^{2221} = \mathcal{R}^{1222} = \mathcal{R}^{2122} = \mathcal{R}^{2212} = 6r^1 + 12r^2 + 3r^3$$

$$\mathcal{R}^{2223} = \mathcal{R}^{2232} = \mathcal{R}^{2322} = \mathcal{R}^{3222} = 3r^1 + 12r^2 + 6r^3$$

$$\mathcal{R}^{3331} = \mathcal{R}^{1333} = \mathcal{R}^{3133} = \mathcal{R}^{3313} = 6r^1 + 3r^2 + 12r^3$$

$$\mathcal{R}^{3332} = \mathcal{R}^{2333} = \mathcal{R}^{3233} = \mathcal{R}^{3323} = 3r^1 + 6r^2 + 12r^3$$

$$\mathcal{R}^{1122} = \mathcal{R}^{1212} = \mathcal{R}^{2112} = \mathcal{R}^{1221} = \mathcal{R}^{2121} = \mathcal{R}^{2211} = 6r^1 + 6r^2 + 2r^3$$

$$\mathcal{R}^{1133} = \mathcal{R}^{1313} = \mathcal{R}^{3113} = \mathcal{R}^{1331} = \mathcal{R}^{3131} = \mathcal{R}^{33111} = 6r^1 + 2r^2 + 6r^3$$

$$\mathcal{R}^{2233} = \mathcal{R}^{2323} = \mathcal{R}^{3223} = \mathcal{R}^{2332} = \mathcal{R}^{3232} = \mathcal{R}^{3322} = 2r^1 + 6r^2 + 6r^3$$

$$\mathcal{R}^{1123} = \mathcal{R}^{1213} = \mathcal{R}^{2113} = \mathcal{R}^{1132} = \mathcal{R}^{1312} = \mathcal{R}^{3112} = \mathcal{R}^{1231} = \mathcal{R}^{2131} = \mathcal{R}^{1321} = \mathcal{R}^{3121} = \mathcal{R}^{2311} = \mathcal{R}^{3211} = 3r^1 + 2r^2 + 2r^3$$

$$\mathcal{R}^{2213} = \mathcal{R}^{2123} = \mathcal{R}^{1223} = \mathcal{R}^{2231} = \mathcal{R}^{2321} = \mathcal{R}^{3221} = \mathcal{R}^{2132} = \mathcal{R}^{1232} = \mathcal{R}^{2312} = \mathcal{R}^{3212} = \mathcal{R}^{1322} = \mathcal{R}^{3122} = 2r^1 + 3r^2 + 2r^3$$

$$\mathcal{R}^{3312} = \mathcal{R}^{3132} = \mathcal{R}^{1332} = \mathcal{R}^{3321} = \mathcal{R}^{3231} = \mathcal{R}^{2331} = \mathcal{R}^{3123} = \mathcal{R}^{1323} = \mathcal{R}^{3213} = \mathcal{R}^{2313} = \mathcal{R}^{1233} = \mathcal{R}^{2133} = 2r^1 + 2r^2 + 3r^3$$

$$\mathcal{K}^{111} = \mathcal{R}^{1111}k^1 + \mathcal{R}^{1112}k^2 + \mathcal{R}^{1113}k^3$$

$$\mathcal{K}^{222} = \mathcal{R}^{2221}k^1 + \mathcal{R}^{2222}k^2 + \mathcal{R}^{2223}k^3$$

$$\mathcal{K}^{333} = \mathcal{R}^{3331}k^1 + \mathcal{R}^{3332}k^2 + \mathcal{R}^{3333}k^3$$

$$\mathcal{K}^{112} = \mathcal{K}^{121} = \mathcal{K}^{211} = \mathcal{R}^{1121}k^1 + \mathcal{R}^{1122}k^2 + \mathcal{R}^{1123}k^3$$

$$\mathcal{K}^{113} = \mathcal{K}^{131} = \mathcal{K}^{311} = \mathcal{R}^{1131}k^1 + \mathcal{R}^{1132}k^2 + \mathcal{R}^{1133}k^3$$

$$\mathcal{K}^{221} = \mathcal{K}^{122} = \mathcal{K}^{212} = \mathcal{R}^{2211}k^1 + \mathcal{R}^{2212}k^2 + \mathcal{R}^{2213}k^3$$

$$\mathcal{K}^{223} = \mathcal{K}^{232} = \mathcal{K}^{322} = \mathcal{K}^{2231}k^1 + \mathcal{R}^{2232}k^2 + \mathcal{R}^{2233}k^3r^3$$

$$\mathcal{K}^{331} = \mathcal{K}^{133} = \mathcal{K}^{313} = \mathcal{R}^{3311}k^1 + \mathcal{R}^{3312}k^2 + \mathcal{R}^{3313}k^3$$

$$\mathcal{K}^{332} = \mathcal{K}^{233} = \mathcal{K}^{323} = \mathcal{R}^{3321}k^1 + \mathcal{R}^{3322}k^2 + \mathcal{R}^{3323}k^3$$

$$\mathcal{K}^{123} = \mathcal{K}^{213} = \mathcal{K}^{132} = \mathcal{K}^{312} = \mathcal{K}^{231} = \mathcal{K}^{321} = \mathcal{R}^{1231}k^1 + \mathcal{R}^{1232}k^2 + \mathcal{R}^{1233}k^3$$

$$\mathcal{H}_j^{11} = \mathcal{K}^{111}c_k^1 + \mathcal{K}^{112}c_k^2 + \mathcal{K}^{113}c_k^3$$

$$\mathcal{H}_j^{22} = \mathcal{K}^{221}c_k^1 + \mathcal{K}^{222}c_k^2 + \mathcal{K}^{223}c_k^3$$

$$\mathcal{H}_j^{33} = \mathcal{K}^{331}c_k^1 + \mathcal{K}^{332}c_k^2 + \mathcal{K}^{333}c_k^3$$

$$\mathcal{H}_j^{12} = \mathcal{H}_j^{21} = \mathcal{K}^{121}c_k^1 + \mathcal{K}^{122}c_k^2 + \mathcal{K}^{123}c_k^3$$

$$\mathcal{H}_j^{13} = \mathcal{H}_j^{31} = \mathcal{K}^{131}c_k^1 + \mathcal{K}^{132}c_k^2 + \mathcal{K}^{133}c_k^3$$

$$\mathcal{H}_j^{23} = \mathcal{H}_j^{32} = \mathcal{K}^{231}c_k^1 + \mathcal{K}^{232}c_k^2 + \mathcal{K}^{233}c_k^3$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \end{array} \right\} = \frac{S}{2520} \left[\begin{array}{cccccc} \mathcal{H}_j^{11} & \mathcal{H}_k^{11} & \mathcal{H}_j^{12} & \mathcal{H}_k^{12} & \mathcal{H}_j^{13} & \mathcal{H}_k^{13} \\ \mathcal{H}_j^{21} & \mathcal{H}_k^{21} & \mathcal{H}_j^{22} & \mathcal{H}_k^{22} & \mathcal{H}_j^{23} & \mathcal{H}_k^{23} \\ \mathcal{H}_j^{31} & \mathcal{H}_k^{31} & \mathcal{H}_j^{32} & \mathcal{H}_k^{32} & \mathcal{H}_j^{33} & \mathcal{H}_k^{33} \end{array} \right] \left\{ \begin{array}{c} c_j^1 \\ c_k^1 \\ c_j^2 \\ c_k^2 \\ c_j^3 \\ c_k^3 \end{array} \right\} \tag{12}$$

2.4.3 Example: monomolecular-monomolecular reversible reaction $A \rightleftharpoons B$

$$v = k_f c_A - k_b c_B$$

$$R_A = -v$$

$$R_B = v$$

$$\left\{\begin{array}{c}\Delta c_A^1\\ \Delta c_B^1\\ \Delta U^1\\ \Delta c_A^2\\ \Delta c_B^2\\ \Delta U^2\\ \Delta c_A^3\\ \Delta c_B^3\\ \Delta U^3\end{array}\right\} = \left[\begin{array}{ccccccccc} -H_A^{11} & H_B^{11} & 0 & -H_A^{12} & H_B^{12} & 0 & -H_A^{13} & H_B^{13} & 0\\ H_A^{11} & -H_B^{11} & 0 & H_A^{12} & -H_B^{12} & 0 & H_A^{13} & -H_B^{13} & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\ -H_A^{21} & H_B^{21} & 0 & -H_A^{22} & H_B^{22} & 0 & -H_A^{23} & H_B^{23} & 0\\ H_A^{21} & -H_B^{21} & 0 & H_A^{22} & -H_B^{22} & 0 & H_A^{23} & -H_B^{23} & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\ -H_A^{31} & H_B^{31} & 0 & -H_A^{32} & H_B^{32} & 0 & -H_A^{33} & H_B^{33} & 0\\ H_A^{31} & -H_B^{31} & 0 & H_A^{32} & -H_B^{32} & 0 & H_A^{33} & -H_B^{33} & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{array}\right] \left\{\begin{array}{c} c_A^1\\ c_B^1\\ U^1\\ c_A^2\\ c_B^2\\ U^2\\ c_A^3\\ c_B^3\\ U^3\end{array}\right\} \tag{13}$$

with for the forward reaction (replace k by k_f in the formulae!)

$$H_A^{mn} = \frac{S}{180}\mathcal{H}_A^{mn}$$

and for the backward reaction (replace k by k_b in the formulae!)

$$H_B^{mn} = \frac{S}{180}\mathcal{H}_B^{mn}$$

2.5 Poisson's equation

2.5.1 Fluctuation in node

$$\begin{aligned}\Delta U^m &= \int_S \vec{\nabla}^2 U N^m r dS + \int_S \tfrac{F}{\epsilon}\sum_i z_i c_i N^m r dS\\ &= -\int_S \vec{\nabla}U.\vec{\nabla}N^m r dS + \sum_i \tfrac{z_i F}{\epsilon}\int_S c_i N^m r dS\end{aligned}$$

2.5.2 Element contribution to fluctuation in node

$$\mathcal{R} = r^1 + r^2 + r^3$$

$$\mathcal{R}^{11} = 6r^1 + 2r^2 + 2r^3$$

$$\mathcal{R}^{22} = 2r^1 + 6r^2 + 2r^3$$

$$\mathcal{R}^{33} = 2r^1 + 2r^2 + 6r^3$$

$$\mathcal{R}^{12} = \mathcal{R}^{21} = 2r^1 + 2r^2 + r^3$$

$$\mathcal{R}^{13} = \mathcal{R}^{31} = 2r^1 + r^2 + 2r^3$$

$$\mathcal{R}^{23} = \mathcal{R}^{32} = r^1 + 2r^2 + 2r^3$$

$$\left\{\begin{array}{c}\Delta U^1\\ \Delta U^2\\ \Delta U^3\end{array}\right\} = \left[\begin{array}{cccccc} \frac{S\mathcal{R}^{11}}{60}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^1.\vec{n}^1}{12S}\mathcal{R} & \frac{S\mathcal{R}^{12}}{60}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^1.\vec{n}^2}{12S}\mathcal{R} & \frac{S\mathcal{R}^{13}}{60}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^1.\vec{n}^3}{12S}\mathcal{R}\\ \frac{S\mathcal{R}^{21}}{60}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^2.\vec{n}^1}{12S}\mathcal{R} & \frac{S\mathcal{R}^{22}}{60}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^2.\vec{n}^2}{12S}\mathcal{R} & \frac{S\mathcal{R}^{23}}{60}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^2.\vec{n}^3}{12S}\mathcal{R}\\ \frac{S\mathcal{R}^{31}}{60}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^3.\vec{n}^1}{12S}\mathcal{R} & \frac{S\mathcal{R}^{32}}{60}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^3.\vec{n}^2}{12S}\mathcal{R} & \frac{S\mathcal{R}^{33}}{60}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^3.\vec{n}^3}{12S}\mathcal{R} \end{array}\right] \left\{\begin{array}{c} c_i^1\\ U^1\\ c_i^2\\ U^2\\ c_i^3\\ U^3\end{array}\right\} \tag{14}$$

2.5.3 Example: binary electrolyte

$$\left\{\begin{array}{c}\Delta c_A^1\\\Delta c_B^1\\\Delta U^1\\\Delta c_A^2\\\Delta c_B^2\\\Delta U^2\\\Delta c_A^3\\\Delta c_B^3\\\Delta U^3\end{array}\right\}=\left[\begin{array}{ccccccccc}0&0&0&0&0&0&0&0&0\\0&0&0&0&0&0&0&0&0\\Z_A^{11}&Z_B^{11}&n^{11}&Z_A^{12}&Z_B^{12}&n^{12}&Z_A^{13}&Z_B^{13}&n^{13}\\0&0&0&0&0&0&0&0&0\\0&0&0&0&0&0&0&0&0\\Z_A^{21}&Z_B^{21}&n^{21}&Z_A^{22}&Z_B^{22}&n^{22}&Z_A^{23}&Z_B^{23}&n^{23}\\0&0&0&0&0&0&0&0&0\\0&0&0&0&0&0&0&0&0\\Z_A^{31}&Z_B^{31}&n^{31}&Z_A^{32}&Z_B^{32}&n^{32}&Z_A^{33}&Z_B^{33}&n^{33}\end{array}\right]\left\{\begin{array}{c}c_A^1\\c_B^1\\U^1\\c_A^2\\c_B^2\\U^2\\c_A^3\\c_B^3\\U^3\end{array}\right\} \tag{15}$$

with

$$Z_i^{mn}=\frac{S\mathcal{R}^{mn}}{60}\frac{z_iF}{\epsilon}$$

$$n^{mn}=-\frac{\vec{n}^m.\vec{n}^n}{12S}\mathcal{R}$$

2.6 Time

2.6.1 Fluctuation in node

$$\Delta c_i^m=\int_S\frac{\partial c_i}{\partial t}N^m r dS$$

2.6.2 Element contribution to fluctuation in node

$$\mathcal{R}^{11}=6r^1+2r^2+2r^3$$

$$\mathcal{R}^{22}=2r^1+6r^2+2r^3$$

$$\mathcal{R}^{33}=2r^1+2r^2+6r^3$$

$$\mathcal{R}^{12}=\mathcal{R}^{21}=2r^1+2r^2+r^3$$

$$\mathcal{R}^{13}=\mathcal{R}^{31}=2r^1+r^2+2r^3$$

$$\mathcal{R}^{23}=\mathcal{R}^{32}=r^1+2r^2+2r^3$$

$$\left\{\begin{array}{c}\Delta c_i^1\\\Delta c_i^2\\\Delta c_i^3\end{array}\right\}=\frac{S}{60}\left[\begin{array}{ccc}\mathcal{R}^{11}&\mathcal{R}^{12}&\mathcal{R}^{13}\\\mathcal{R}^{21}&\mathcal{R}^{22}&\mathcal{R}^{23}\\\mathcal{R}^{31}&\mathcal{R}^{32}&\mathcal{R}^{33}\end{array}\right]\left\{\begin{array}{c}\frac{\partial c_i^1}{\partial t}\\\frac{\partial c_i^2}{\partial t}\\\frac{\partial c_i^3}{\partial t}\end{array}\right\} \tag{16}$$

3 Boundary element vector

3.1 Electrode reactions

3.1.1 Fluctuation in node

$$R_i = \sum_r s_{i,r} v_r$$

$$v = k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right] c_{red} - k_{red} \exp\left[-\frac{\alpha_{red} nF}{RT}(V-U)\right] c_{ox}$$

$$\Delta c_i^m = \int_L R_i N^m r dL$$

3.1.2 Boundary element contribution to fluctuation in node

Assume that the normal flux varies linearly on the boundary.

$$\mathcal{R}^{11} = 3r^1 + r^2$$

$$\mathcal{R}^{22} = r^1 + 3r^2$$

$$\mathcal{R}^{12} = \mathcal{R}^{21} = r^1 + r^2$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \end{array} \right\} = \frac{L}{12} \left\{ \begin{array}{c} \mathcal{R}^{11} R_i^1 + \mathcal{R}^{12} R_i^2 \\ \mathcal{R}^{21} R_i^1 + \mathcal{R}^{22} R_i^2 \end{array} \right\} \tag{17}$$

3.1.3 Example: binary electrolyte, $A \rightleftharpoons B + ne^-$

$$v = k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right] c_B - k_{red} \exp\left[-\frac{\alpha_{red} nF}{RT}(V-U)\right] c_A$$

$$R_A = -v$$

$$R_B = v$$

$$\left\{ \begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \end{array} \right\} = \left\{ \begin{array}{c} -\frac{L}{12}\left(\mathcal{R}^{11} v^1 + \mathcal{R}^{12} v^2\right) \\ \frac{L}{12}\left(\mathcal{R}^{11} v^1 + \mathcal{R}^{12} v^2\right) \\ 0 \\ -\frac{L}{12}\left(\mathcal{R}^{21} v^1 + \mathcal{R}^{22} v^2\right) \\ \frac{L}{12}\left(\mathcal{R}^{21} v^1 + \mathcal{R}^{22} v^2\right) \\ 0 \end{array} \right\} \tag{18}$$

4 Element jacobian

4.1 Convection

Zero contribution.

4.2 Diffusion

Zero contribution (approximately).

4.3 Migration

4.3.1 Element contribution to fluctuation in node

$$\vec{\nabla} U = \frac{\vec{n}^1 U^1 + \vec{n}^2 U^2 + \vec{n}^3 U^3}{2S}$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \end{array} \right\} = -\frac{\vec{\nabla} U}{120} . \left[\begin{array}{ccc} \vec{n}^1 \mathcal{W}_i^1 & \vec{n}^1 \mathcal{W}_i^2 & \vec{n}^1 \mathcal{W}_i^3 \\ \vec{n}^2 \mathcal{W}_i^1 & \vec{n}^2 \mathcal{W}_i^2 & \vec{n}^2 \mathcal{W}_i^3 \\ \vec{n}^3 \mathcal{W}_i^1 & \vec{n}^3 \mathcal{W}_i^2 & \vec{n}^3 \mathcal{W}_i^3 \end{array} \right] \left\{ \begin{array}{c} c_i^1 \\ c_i^2 \\ c_i^3 \end{array} \right\} \tag{19}$$

4.3.2 Example: binary electrolyte

$$\left\{ \begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \\ \Delta c_A^3 \\ \Delta c_B^3 \\ \Delta U^3 \end{array} \right\} = \left[\begin{array}{ccccccccc} \tilde{M}_A^{11} & 0 & 0 & \tilde{M}_A^{12} & 0 & 0 & \tilde{M}_A^{13} & 0 & 0 \\ 0 & \tilde{M}_B^{11} & 0 & 0 & \tilde{M}_B^{12} & 0 & 0 & \tilde{M}_B^{13} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \tilde{M}_A^{21} & 0 & 0 & \tilde{M}_A^{22} & 0 & 0 & \tilde{M}_A^{23} & 0 & 0 \\ 0 & \tilde{M}_B^{21} & 0 & 0 & \tilde{M}_B^{22} & 0 & 0 & \tilde{M}_B^{23} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \tilde{M}_A^{31} & 0 & 0 & \tilde{M}_A^{32} & 0 & 0 & \tilde{M}_A^{33} & 0 & 0 \\ 0 & \tilde{M}_B^{31} & 0 & 0 & \tilde{M}_B^{32} & 0 & 0 & \tilde{M}_B^{33} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{array} \right] \left\{ \begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \\ c_A^3 \\ c_B^3 \\ U^3 \end{array} \right\} \tag{20}$$

with

$$\tilde{M}_i^{mn} = -\vec{\nabla} U . \vec{n}^m \frac{\mathcal{W}_i^n}{120}$$

4.4 Homogeneous reactions

4.4.1 Element contribution to fluctuation in node

- Monomolecular

Zero contribution (approximately).

- Bimolecular

Because of the symmetry it is the same contribution.

$$\left\{\begin{array}{c}\Delta c_i^1\\ \Delta c_i^2\\ \Delta c_i^3\end{array}\right\} = \frac{S}{2520}\left[\begin{array}{cccccc}\mathcal{H}_j^{11} & \mathcal{H}_k^{11} & \mathcal{H}_j^{12} & \mathcal{H}_k^{12} & \mathcal{H}_j^{13} & \mathcal{H}_k^{13}\\ \mathcal{H}_j^{21} & \mathcal{H}_k^{21} & \mathcal{H}_j^{22} & \mathcal{H}_k^{22} & \mathcal{H}_j^{23} & \mathcal{H}_k^{23}\\ \mathcal{H}_j^{31} & \mathcal{H}_k^{31} & \mathcal{H}_j^{32} & \mathcal{H}_k^{32} & \mathcal{H}_j^{33} & \mathcal{H}_k^{33}\end{array}\right]\left\{\begin{array}{c}c_j^1\\ c_k^1\\ c_j^2\\ c_k^2\\ c_j^3\\ c_k^3\end{array}\right\} \tag{21}$$

4.5 Poisson's equation

Zero contribution.

4.6 Time

Zero contribution.

5 Boundary element jacobian

5.1 Electrode reactions

5.1.1 Partial derivatives

$$\frac{\partial v}{\partial U} = -\frac{\alpha_{ox}nF}{RT}k_{ox}\exp\left[\frac{\alpha_{ox}nF}{RT}(V-U)\right]c_{red} - \frac{\alpha_{red}nF}{RT}k_{red}\exp\left[-\frac{\alpha_{red}nF}{RT}(V-U)\right]c_{ox}$$

$$\frac{\partial v}{\partial c_{ox}} = -k_{red}\exp\left[-\frac{\alpha_{red}nF}{RT}(V-U)\right]$$

$$\frac{\partial v}{\partial c_{red}} = k_{ox}\exp\left[\frac{\alpha_{ox}nF}{RT}(V-U)\right]$$

$$\left\{\begin{array}{c}\Delta c_i^1\\ \Delta c_i^2\end{array}\right\} = \frac{L}{12}\left[\begin{array}{cccc}\mathcal{R}^{11}\frac{\partial R_i^1}{\partial c_j^1} & \mathcal{R}^{11}\frac{\partial R_i^1}{\partial U^1} & \mathcal{R}^{12}\frac{\partial R_i^2}{\partial c_j^2} & \mathcal{R}^{12}\frac{\partial R_i^2}{\partial U^2}\\ \mathcal{R}^{21}\frac{\partial R_i^1}{\partial c_j^1} & \mathcal{R}^{21}\frac{\partial R_i^1}{\partial U^1} & \mathcal{R}^{22}\frac{\partial R_i^2}{\partial c_j^2} & \mathcal{R}^{22}\frac{\partial R_i^2}{\partial U^2}\end{array}\right]\left\{\begin{array}{c}c_j^1\\ U^1\\ c_j^2\\ U^2\end{array}\right\} \tag{22}$$

5.1.2 Example: binary electrolyte, $A \rightleftharpoons B + ne^-$

$$\frac{\partial v}{\partial U} = -\frac{\alpha_{ox}nF}{RT}k_{ox}\exp\left[\frac{\alpha_{ox}nF}{RT}(V-U)\right]c_B - \frac{\alpha_{red}nF}{RT}k_{red}\exp\left[-\frac{\alpha_{red}nF}{RT}(V-U)\right]c_A$$

$$\frac{\partial v}{\partial c_A} = -k_{red}\exp\left[-\frac{\alpha_{red}nF}{RT}(V-U)\right]$$

$$\frac{\partial v}{\partial c_B} = k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right]$$

$$\left\{\begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \end{array}\right\} = \left[\begin{array}{cccccc} -\tilde{C}_A^{11} & -\tilde{C}_B^{11} & -\tilde{U}^{11} & -\tilde{C}_A^{12} & -\tilde{C}_B^{12} & -\tilde{U}^{12} \\ \tilde{C}_A^{11} & \tilde{C}_B^{11} & \tilde{U}^{11} & \tilde{C}_A^{12} & \tilde{C}_B^{12} & \tilde{U}^{12} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -\tilde{C}_A^{21} & -\tilde{C}_B^{21} & -\tilde{U}^{21} & -\tilde{C}_A^{22} & -\tilde{C}_B^{22} & -\tilde{U}^{22} \\ \tilde{C}_A^{21} & \tilde{C}_B^{21} & \tilde{U}^{21} & \tilde{C}_A^{22} & \tilde{C}_B^{22} & \tilde{U}^{22} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{array}\right] \left\{\begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \end{array}\right\} \tag{23}$$

with

$$\tilde{C}_i^{mn} = \frac{L\mathcal{R}^{mn}}{12}\frac{\partial v^n}{\partial c_i^n}$$

$$\tilde{U}^{mn} = \frac{L\mathcal{R}^{mn}}{12}\frac{\partial v^n}{\partial U^n}$$